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ORTHOGONAL SELF-ASSEMBLY OF REDOX ACTIVE MOLECULES ON PT AND AU:
SELECTIVE REACTION OF DISULFIDE WITH AU AND ISONITRILE WITH PT

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Technical Report No. 46 (February 1992)

Interim Technical Report
(Accepted for publication in Langmuir)

PREPARED FOR DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
1400 Wilson Boulevard
Arlington VA 22209

DEPARTMENT OF THE NAVY
Office of Naval Research, Code 1130P
800 North Quincy Street
Arlington VA 22217-5000

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Project No.: a400011dd205
Contract No.: N00014-86-K-0756
Effective Date: 86 September 15
Expiration Date: 92 September 14

Principal Investigator: George M. Whitesides
(617) 495-9430

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92 2 14 128

92-04272



REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 46			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Harvard University		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION DARPA		
6c. ADDRESS (City, State, and ZIP Code) Office for Sponsored Research Holyoke Center, Fourth Floor Cambridge MA 02138-4993			7b. ADDRESS (City, State, and ZIP Code) 1400 Wilson Boulevard Arlington VA 22209-2308		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division, Code 1113 Office of Naval Research Arlington VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 86-K-0756	PROJECT NO.	TASK NO. a400011dd2
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Orthogonal Self-Assembly of Redox Active Molecules on Pt and Au: Selective Reaction of Disulfide with Au and Isonitrile with Pt					
12. PERSONAL AUTHOR(S) J.J. Hickman, P.E. Laibinis, D.I. Auerbach, C. Zou, T.J. Gardner, G.M. Whitesides, & M.G. Hight					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day)	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>Surfaces of platinum and gold adsorb ferrocenyl-12-dodecyl isocyanide, I, and di(10-ferrocenecarbonyl-decyl)disulfide, II, and yield self-assembled, redox active monolayers incorporating ferrocene groups. The values of $E_{1/2}$ for alkyl ferrocenyl centers from I are ~300 mV more negative than acyl ferrocenyl centers from II. This difference allows easy electrochemical measurement of</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold Guard			22b. TELEPHONE (Include Area Code) 202/696-4409		22c. OFFICE SYMBOL

surface concentrations of ferrocene centers from I and II on Pt or Au. I adsorbs selectively on Pt or Au compared to II, but with different degrees of selectivity. Further, for Pt the selectivity depends on the surface pretreatment. The affinity of II for a Pt surface first exposed to an O₂ plasma (oxidized Pt) is lower than that for a Pt surface exposed first to an O₂ plasma and then to a H₂ plasma (reduced Pt). The same two plasma treatments of Pt do not affect the binding of I on Pt. Thus, the selectivity of Pt for I vs. II is higher for the oxidized Pt (~200:1) compared to that for the reduced Pt (~20:1). The two plasma treatments of Au do not influence the selectivity for binding I vs. II; the selectivity for binding I vs. II on Au is ~8:1. By using the O₂ plasma pretreatment and a 40:1 solution of II:I, orthogonal self-assembly of II onto Au and I onto Pt can be effected when the two samples are derivatized in the same solution. The orthogonal self-assembly yields a 1:10 ratio and a 10:1 ratio of the alkyl ferrocenyl:acyl ferrocenyl centers on Au and Pt surfaces, respectively.

Orthogonal Self-Assembly of Redox Active Molecules on Pt
and Au: Selective Reaction of Disulfide With Au and
Isonitrile with Pt

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Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
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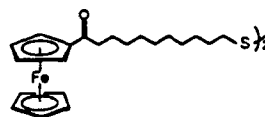
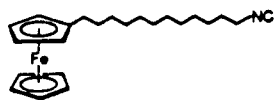
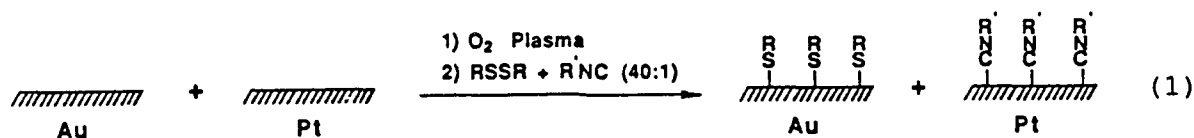
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Abstract

Surfaces of platinum and gold adsorb ferrocenyl-12-dodecyl isocyanide, **I**, and di(10-ferrocenecarbonyl-decyl)disulfide, **II**, and yield self-assembled, redox active monolayers incorporating ferrocene groups. The values of $E_{1/2}$ for alkyl ferrocenyl centers from **I** are ~300 mV more negative than acyl ferrocenyl centers from **II**. This difference allows easy electrochemical measurement of surface concentrations of ferrocene centers from **I** and **II** on Pt or Au. **I** adsorbs selectively on Pt or Au compared to **II**, but with different degrees of selectivity. Further, for Pt the selectivity depends on the surface pretreatment. The affinity of **II** for a Pt surface first exposed to an O₂ plasma (oxidized Pt) is lower than that for a Pt surface exposed first to an O₂ plasma and then to a H₂ plasma (reduced Pt). The same two plasma treatments of Pt do not affect the binding of **I** on Pt. Thus, the selectivity of Pt for **I** vs. **II** is higher for the oxidized Pt (~200:1) compared to that for the reduced Pt (~20:1). The two plasma treatments of Au do not influence the selectivity for binding **I** vs. **II**; the selectivity for binding **I** vs. **II** on Au is ~8:1. By using the O₂ plasma pretreatment and a 40:1 solution of **II**:**I**, orthogonal self-assembly of **II** onto Au and **I** onto Pt can be effected when the two samples are derivatized in the same solution. The orthogonal self-assembly yields a 1:10 ratio and a 10:1 ratio of the alkyl ferrocenyl:acyl ferrocenyl centers on Au and Pt surfaces, respectively.

We wish to report procedures for formation of self-assembled monolayers that modify Au and Pt electrodes selectively when both are immersed in a common solution containing the isonitrile, **I**, and the disulfide, **II**, equation (1). Much work has been reported



recently concerning the use of self-assembly methods to functionalize electrode surfaces.¹⁻¹¹ Relatively little work, however, has been reported concerning the self-assembly of multi-component systems on different substrates. We have named selectivity of the sort represented in equation (1) "orthogonal self-assembly",¹² meaning that each molecule adsorbs selectively to a different surface. We have previously demonstrated such orthogonal self-assembly for Au and Al₂O₃: thiols selectively bind to Au, and carboxylic acids bind selectively to Al₂O₃.¹² Part of the significance of our new findings is that both Pt and Au are useful electrode materials, whereas insulating Al₂O₃ is not. Thus, orthogonal self-assembly using **I** and **II** can be exploited to

prepare an organized two-component, redox active molecular assembly.

Self-assembly of redox active monolayers has been accomplished by immersion of Pt and/or Au into organic solutions of **I**¹³ and/or **II**.^{14,15} The $E_{1/2}$ for the alkyl ferrocenyl centers from **I** is ~300 mV more negative than $E_{1/2}$ for the acyl ferrocenyl centers from **II**, allowing easy electrochemical measurement of their surface concentrations even when both species are on the surface. For Au or Pt surfaces pretreated by sequential exposure to an O₂ plasma (2-5 min) followed a H₂ plasma (1 min), we find that **I** or **II** form a durable, redox active monolayer ($3-5 \times 10^{-10}$ mol/cm²) on either Pt or Au. However, pretreatment with only the O₂ plasma suppresses the uptake of **II** on Pt, while not affecting the uptake of **I**, Figure 1. The pretreatment procedure involving only the O₂ plasma for Au gives the same response to **I** or **II** as found when pretreatment involves the sequential O₂ and H₂ plasmas. X-ray photoelectron spectra in the 4f_{7/2} region, Figure 2, show high binding energy peaks consistent with the presence of a Au or Pt oxide after the O₂ plasma pretreatment which is removed by the H₂ plasma pretreatment.¹⁶

Ten independent comparisons show that the reduced Pt (O₂ plasma followed by H₂ plasma) yields about ten times the coverage of redox active material as does the oxidized Pt (O₂ plasma only) when reacting both surfaces in the same solution of **II**, Figure 1. Importantly, oxidized and reduced Pt derivatized with only **I** show the same coverage, $\sim 4 \pm 1 \times 10^{-10}$ mol/cm². XPS analysis of oxidized Pt functionalized with **I** shows high binding energy Pt

4f_{7/2} peaks, consistent with retention of the oxidized surface. In contrast, XPS of oxidized Au after reaction with I or II shows no detectable high binding energy peaks, consistent with loss of the Au oxide. Electrochemically formed Au oxide has been shown to be reactive toward other surface modification reagents.¹⁷

Electrochemical analyses of pretreated Pt and Au after reaction with mixtures of I and II show that I is always more competitively adsorbed than II, but a sufficiently large ratio of II:I in solution will yield selective uptake of II. The reduced and oxidized Au both give a preference of I vs. II of 8:1. Reduced and oxidized Pt, however, have different preferences for I vs. II, since oxidized Pt is nearly inert to II. The preferences for uptake of I vs. II on oxidized and reduced Pt are ~200:1 and ~20:1, respectively. Thus, pretreatment of Pt and Au with only the O₂ plasma is predicted to give the highest degree of orthogonal self-assembly by reaction with I and II with Pt and Au.

By using a 40:1 ratio of II:I in solution and the O₂ plasma pretreatment of Au and Pt, we have demonstrated selective functionalization of Pt with I and selective functionalization of Au with II when derivatized in the same solution of I and II. The orthogonal self-assembly yields a 1:10 and 10:1 ratio of alkyl ferrocenyl:acyl ferrocenyl centers on Au and Pt, respectively, Figure 3. The total coverage of ferrocene centers is always $4 \pm 1 \times 10^{-10}$ mol/cm², or about one monolayer. Changing the ratio of I and II in solution changes the ratio of the two different centers on the Au and Pt surfaces in a manner consistent with a competitive reaction of I and II. Further studies are underway to

establish the scope of orthogonal self-assembly on Pt and Au, in order to functionalize microelectrode arrays^{12,13} with a variety of redox centers.

Acknowledgement. We thank the Office of Naval Research and the Defense Advanced Research Projects Agency for partial support of this research. We acknowledge use of XPS and Auger facilities acquired through the joint Harvard/M.I.T. University Research Initiative funded by the Defense Advanced Research Projects Agency.

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15. Prior to derivatization the e⁻-beam evaporated Au and/or Pt on a Si substrate was pretreated with an O₂ plasma (2-5 min) or with the O₂ plasma followed by a H₂ plasma (1 min). Plasma treatment was done using a Harrick PDC-23G plasma cleaner. The O₂ treatment was at 0.3 torr at medium power (60 W) and the H₂ treatment was at 0.3 torr at low power (40 W). Immediately after a plasma pretreatment, the electrodes were derivatized by immersion into a deoxygenated 5 x 10⁻⁵ M solution of I or into a 10⁻⁴ M solution of II in 1:1 EtOH:hexane solvent. Best results for orthogonal self-assembly were achieved using the O₂ plasma pretreatment and a 40:1 solution of II:I in 1:1 EtOH:hexane as solvent at total concentration of adsorbate of 10⁻⁴ M. Typical derivatization times were 18-48 h.

16. XPS was done using an SSL 100 spectrometer. Samples were attached to the stage via metal clips. The lowest energy Pt 4f_{7/2} peak was taken to be Pt(0) and the lowest energy Au 4f_{7/2} peak was taken to be Au(0), and they were monitored as the references to correct any peak shifts due to sample charging (Au(0) 4f_{7/2} is at 84.0 eV and Pt(0) 4f_{7/2} is at 71.0 eV binding energy). The X-ray line used for excitation was the Al K α line at 1486.6 eV. For a general reference, see: Handbook of X-ray Photoelectron Spectroscopy, published by Perkin-Elmer Corp., Eden, Prairie, MN., 1979.

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Figure Captions

Figure 1. Cyclic voltammetry (500 mV/s) in $\text{CH}_3\text{CN}/0.1 \text{ M}$ $[\text{n-Bu}_4\text{N}]\text{PF}_6$ for Pt electrodes after modification by reaction with $5 \times 10^{-5} \text{ M I}$ (top) or with 10^{-4} M II (bottom) for 18 h in $\text{EtOH}:\text{hexane}$ (1:1). The data on the left are for Pt electrodes pretreated with a 2 min O_2 plasma and the data on the right are for Pt electrodes pretreated with a 3 min O_2 plasma followed by 1 min H_2 plasma.

Figure 2. Comparison of XPS spectra for Pt and Au pretreated with a 3 min O_2 plasma or with a 3 min O_2 plasma followed by a 1 min H_2 plasma.

Figure 3. Comparison of cyclic voltammetry (500 mV/s) in $\text{CH}_3\text{CN}/0.1 \text{ M}$ $[\text{n-Bu}_4\text{N}]\text{PF}_6$ for oxidized (2 min O_2 plasma pretreatment) Pt and Au electrodes after derivitization in $\text{EtOH}:\text{hexane}$ (1:1) solution containing $1 \times 10^{-4} \text{ M II}$ and $2.5 \times 10^{-6} \text{ M I}$ for 18 h.

